

Electrochemical performance and thermal property of electrospun PPESK/PVDF/PPESK composite separator for lithium-ion battery

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Abstract In this study, PPESK/PVDF/PPESK tri-layer composite separators for lithium-ion batteries were prepared by electrospinning technique. The physical properties, electrochemical performances and thermal properties of composite separators were investigated. Results indicate that PPESK/PVDF/PPESK separator displays good wettability in liquid electrolyte. The electrolyte uptake of PPESK/PVDF/PPESK separator is much higher than that of electrospun PVDF, which leads to higher ionic conductivity of PPESK/PVDF/PPESK separator than PVDF separator. Discharge capacity of the cell assembled with PPESK/PVDF/PPESK separator is increased by 50 % than that with PVDF separator. Initial charge–discharge efficiency and capacity retention property of the cell with PPESK/PVDF/PPESK are better than those with PVDF separator or PPESK separator. In addition, when the mass ratio between PPESK and PVDF resins is increased to 4:3, PPESK/PVDF/PPESK

separators show good thermal dimensional stability even thermally treated at 180 °C for 1 h.

Keywords Poly(phthalazinone ether sulfone ketone) · Poly(vinylidene fluoride) · Composite separator · Electrospinning · Lithium-ion battery · Thermal dimensional stability

1 Introduction

The separator as one of the important components for lithium-ion battery is used to separate positive and negative electrodes and maintain the liquid electrolyte between both of electrodes. The thermal dimensional stability and wettability in liquid electrolyte of the separators play very important roles on thermal safety and electrochemical performance of the batteries [1, 2]. Currently, Polyolefin microporous membranes have been used as major separators for lithium-ion batteries. However, the polyolefin microporous membranes often show low ionic conductivity due to poor wettability and low porosity (about 40 %). The rate capability of battery with polyolefin separator is not enough for high-power applications. To improve the electrochemical properties, new kinds of separators have been developed, such as polymer electrolyte separator, gel-polymer electrolyte separator, electrospun nonwoven separator and so on [3–5]. In all kinds of separators, electrospun nonwoven separators display relatively higher specific surface area and porosity (60–90 %) because of their dimensional network structure, which can largely reduce battery resistance and increase the rate capability of battery [1, 6–8]. Some electrospun polymer nonwoven fabrics, such as electrospun Poly(ethylene oxide) (PEO), Polyacrylonitrile (PAN), Poly(methyl methacrylate) (PMMA),

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Poly(vinylidene fluoride) (PVDF) and Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) fabrics, have been used as polymer electrolyte separators in lithium-ion batteries. And electrochemical properties of the batteries with these electrospun separators were improved in varying degrees [3–5, 9–11]. However, when the battery thermorunaway occurs, these separators easily shrink or melt because of relatively low melting temperature (<250 °C) of the materials, which might lead to potential safety issues. To improve the thermal safety of lithium ionic batteries, polyolefin tri-layer composite separators-Celgard® 2325 separator (PP/PE/PP) is designed by PP and PE materials [12–14]. When the thermorunaway occurs, the middle layer (PE) of the separator melts firstly. The pores of the separator are blocked up. Hence, the internal current is cut down, which prevents further electrochemical reaction. Similarly, some novel electrospun tri-layer separators have been developed to improve thermal safety, such as PVDF/PMMA/PVDF composite separators, PVDF/PAN/PVDF composite separators and so on [5, 9, 12]. However, despite the tri-layer composite separators have shutdown characteristic, the temperature of the batteries cannot keep from rising up as soon as the current is cut down. Potential safety hazard still exists due to poor thermal dimensional stability of separators, especially for the batteries used in severe environment. Therefore, it is necessary to develop new separator materials with high thermal dimensional stability.

Poly(phthalazinone ether sulfone ketone) (PPESK) is a novel kind of soluble thermoplastic resins with excellent thermal resistance property and good chemical stability. The glass-transition temperature of PPESK is ranging from 263 to 305 °C [15–17]. In our previous work, electrospun PPESK nonwoven fabrics have been successfully prepared and used as separators for lithium-ion batteries [18, 19]. The results indicate that electrospun PPESK fabrics have excellent thermal dimensional stability and good wettability in liquid electrolyte. However, in some of our subsequent experiments, the batteries assembled with electrospun PPESK fabrics occasionally display unstable discharge capacity during cycling tests. This unstable discharge performance might result from large pore size and excessively high porosity of electrospun PPESK fabrics. Thus, a modification on electrospun PPESK fabrics is necessary to improve the electrochemical cycling properties of batteries. Recently, PVDF resins and its copolymers (PVDF-HFP, PVDF-TrFE and PVDF-CTFE) have become favorable matrixes for polymer electrolyte for lithium-ion batteries [20, 21]. Many researches have demonstrated that PVDF and its copolymers separator/electrolyte systems show good wettability and high ionic conductivity. The cells assembled with these porous separators display good electrochemical performances [20–26]. However, thermal dimensional stability of

PVDF and its copolymers separators is not enough for high-performance batteries due to their low melting points.

In this study, PPESK/PVDF/PPESK tri-layer composite separators were prepared by using electrospinning technique. The morphology, physical properties, electrochemical performances and thermal properties of the composite separators were investigated.

2 Experimental

2.1 Materials

PPESK resins were obtained from Dalian Polymer New Material Co., Ltd. (Dalian, China). PVDF resins were purchased from Shanghai Ofluorine Chemical Technology Co., Ltd. (Shanghai, China). Acetone and *N,N*-dimethylacetamide (DMAc) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 1 mol L⁻¹ LiPF₆-EC/DMC (1:1 in volume) electrolyte was obtained from Shantou Jinguang High Tech Co., Ltd. (Guangdong, China).

2.2 Preparation of the electrospun PPESK/PVDF/PPESK composite membrane

A total of 20 wt% PPESK/DMAc solutions and 15 wt% PVDF/(DMAc/acetone) ($V_{\text{DMAc}}:V_{\text{Acetone}} = 3:7$) solutions were used to prepare three kinds of electrospun PPESK/PVDF/PPESK composite separators with different mass ratios between PPESK and PVDF resins. The mass ratios (PPESK: PVDF) of the three composite separators were 2:3, 4:3 and 8:3, respectively. Electrospinning of PPESK/PVDF/PPESK composite separator was performed as below. Firstly, 23 kV high voltage was provided for electrospinning of 0.3 mL PPESK/DMAc solutions with 4.2 mL h⁻¹ flow rate and at 10 cm distance between needle tip and collecting drum; secondly, PVDF/(DMAc/acetone) solutions of appropriate volume were electrospun on the PPESK fabrics with 25 kV high voltage, 2.8 mL h⁻¹ flow rate at 15 cm distance between needle tip and collecting drum; finally, 0.3 mL PPESK solutions were electrospun on the PVDF fabrics with 23 kV high voltage at 10 cm distance between needle tip and collecting drum. The collecting linear velocity throughout the whole electrospinning process was about 3.15 m s⁻¹. For comparison, the electrospun PPESK fabrics and PVDF fabrics were also prepared. All the separators were dried at 120 °C for 6 h.

2.3 Membrane characterization

Fiber morphologies of the electrospun PPESK and PVDF fabrics were characterized by scanning electron microscopy

(SEM, Quanta 200, FEI). Fiber diameter was determined by analysis of SEM images manually. Image analysis software was used to measure the pore area from the SEM image. The pore area on the surface of electrospun fabrics was measured by image analysis software under automatically thresholding state of the SEM image of fabrics. The pore size was characterized by the equivalent diameter, which is described as the diameter of a circle with identical area. The average pore size (APS) was calculated by the equivalent diameter of the seventy pores at least [11]. Thickness of separators was measured by thin-film pachymeter (Chengdu Chengliang Instrument. Co. Ltd. Chengdu, China) at least three times. Thermal properties of PPESK/PVDF/PPESK separator were evaluated using differential scanning calorimetry (DSC, Diamond) from 50 to 320 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

The separators were soaked in 1 mol L⁻¹ LiPF₆-EC/DMC for 2 h to characterize electrolyte uptake, which was calculated according to the Eq. (1) [3]:

$$\text{uptake} = \frac{W_a - W_b}{W_b} \times 100 \% \quad (1)$$

where W_a and W_b are the mass of separator after and before immersion in liquid electrolyte, respectively.

Porosity of separator was determined using *n*-butanol uptake. The separators were immersed in *n*-butanol for 2 h. Filter papers were used to remove the *n*-butanol on the separators' surface. The masses of separator before and after immersion were measured [26, 27]. The porosity was calculated using the Eq. (2):

$$\text{porosity} = \frac{(m_a - m_p)/\rho_b}{(m_a - m_p)/\rho_b + m_p/\rho_p} \times 100 \% \quad (2)$$

Where m_a and m_p are the masses of separator after and before immersion in *n*-butanol, ρ_b is the density of *n*-butanol, and ρ_p is the density of polymer.

2.4 Ionic conductivity

The ionic conductivity of separator/electrolyte was measured by AC impedance spectroscopy using electrochemical workstation (CHI660C, Shanghai Chenhua Instrument. Co. Ltd. China) over the frequency ranging from 1 Hz to 100 kHz with 5 mV of AC amplitude. The soaked separator was sandwiched between two stainless steel spacers (SS/separator/SS system) and sealed in CR2032 coin cell shells. The ionic conductivity of the separator (σ) was calculated using the Eq. (3) [9]:

$$\sigma = \frac{d}{R_b S} \quad (3)$$

Where σ is the ionic conductivity, d is the thickness of the membrane, R_b is the bulk resistance of soaked separator and S is the area of the symmetrical electrode, respectively.

2.5 Electrochemical properties

The charge–discharge cycling of the cells were conducted by a battery cycler (CT2001A, Wuhan Jinnuo Electronics Co., Ltd, China). CR2032 coin cells were assembled with LiCoO₂ electrode as a cathode, graphite electrode as an anode and a separator with 1 mol L⁻¹ LiPF₆-EC/DMC as electrolyte. The electrochemical cycles of the cells were evaluated under constant current–constant voltage (CC–CV) charge mode and constant current discharge mode, with a cutoff potential of 2.8 and 4.2 V at room temperature. The initial cycle was carried out at 0.2 C rate, and the following cycles were carried out at 0.5 C rate.

3 Results and discussion

3.1 Morphologies of PPESK/PVDF/PPESK composite separator

Figure 1 shows the side structure and surface morphology of PPESK/PVDF/PPESK composite separator. As shown in Fig. 1a, PPESK/PVDF/PPESK composite separator consists of three layers. The thin PVDF fabrics were sandwiched by two PPESK fabrics layers, which display fluffy morphology. The fiber diameter distribution histograms of electrospun PPESK fabrics and PVDF fabrics are shown in Fig. 1b, c, respectively. As is visually observed from the inserted SEM images, PPESK fabrics show larger pore size and fiber diameter than PVDF fabrics. In addition, the diameter distribution of PPESK fabrics seems more uniform than that of PVDF fabrics. Further analysis is summarized in Table 1. It shows that the average pore size (APS) of PPESK fabrics is larger than that of PVDF fabrics. The average fiber diameters (AFD) of PPESK and PVDF fabrics are 1.38 and 0.92 μm, respectively. And PPESK fabrics have narrower diameter distribution width than PVDF fabrics.

3.2 Physical characterization of PPESK/PVDF/PPESK composite separator

The electrolyte uptakes of different PPESK/PVDF/PPESK composite separators were investigated. The electrolyte uptakes of electrospun PVDF and PPESK fabrics were also measured for comparison. The theoretical uptakes of the PPESK/PVDF/PPESK composite separators are calculated according to the practical uptakes of PVDF fabrics and PPESK fabrics. The results are listed in Table 1. PPESK fabrics show highest electrolyte uptake in all separators. The PPESK/PVDF/PPESK separators display about two times higher electrolyte uptake than the PVDF separators. Moreover, both practical and theoretical electrolyte uptakes of composite separators increase while increasing PPESK content. Usually, high electrolyte uptakes result from high

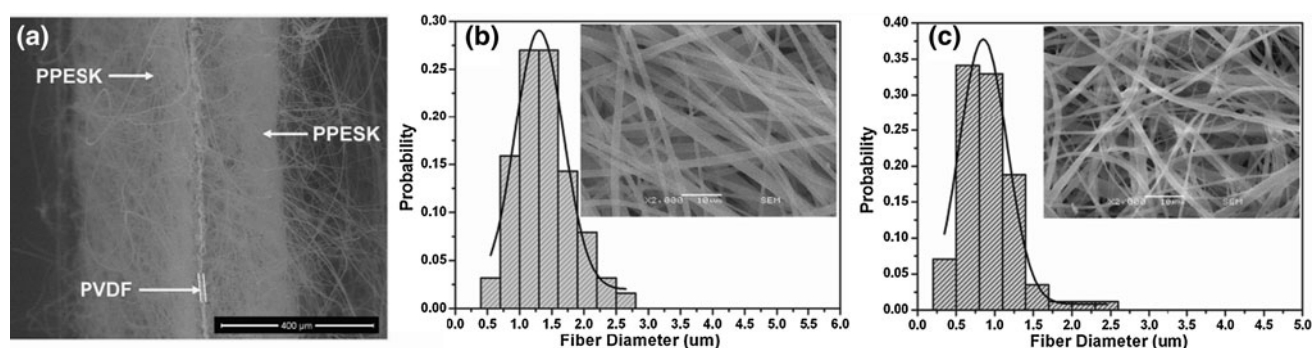


Fig. 1 SEM images and fiber diameter distribution histograms of electrospun fabric separators, (a) side view of PPESK/PVDF/PPESK composite separator; (b) PPESK fabrics; (c) PVDF fabrics

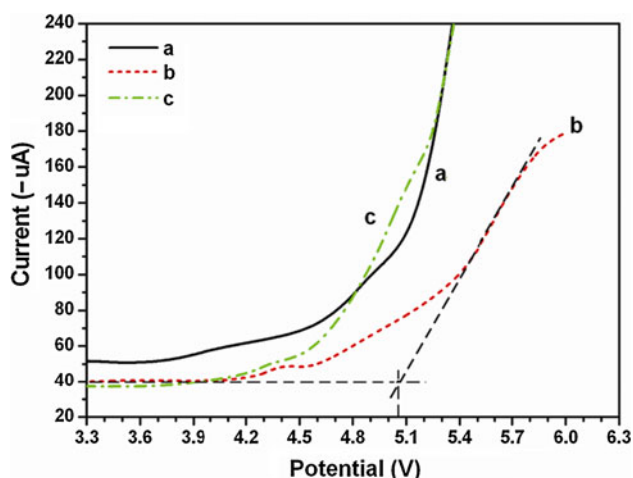


Fig. 2 Current–voltage curves of different separator/electrolyte systems, (a) PVDF separator/electrolyte; (b) PPESK separator/electrolyte; (c) PPESK/PVDF/PPESK composite separator/electrolyte

porosity and good wettability of separators. As shown in Table 1, both PVDF fabrics and PPESK fabrics display high porosity of about 90 % due to their small fiber diameter and three-dimensional network structure [10, 23, 28–32]. However, the electrolyte uptake of PPESK fabrics is nearly three

times higher than that of PVDF fabrics despite of similar porosity. Such different uptake between PPESK and PVDF separators indicates that the wettability in liquid electrolyte plays a more important role than porosity on improving the electrolyte uptake of separators. As is known, PVDF, a semi-crystalline polymer, easily forms crystalline phase, during the electrospinning process [33]. And high crystallinity of PVDF negatively affects the electrolyte uptake of the separator [34, 35]. Instead, PPESK as a kind of amorphous polymers has many polar chemical bonds in its molecular structure, such as C=O, S=O and –O– bonds [15–17]. PPESK display more similar polarity with carbonic ester liquid electrolyte than PVDF. Thus, PPESK fabrics show better wettability in liquid electrolyte (1 mol L⁻¹ LiPF₆-EC/DMC) than PVDF fabrics. Besides, it is worthy to note that the practical electrolyte uptake of the composite separators is higher than the theoretical, which could result from puffed interface between PVDF fabrics and PPESK fabrics in the composite separators.

3.3 Ionic conductivity of PPESK/PVDF/PPESK composite separator

High electrolyte uptake of separator is beneficial to improving ionic conductivity of separator/electrolyte [36].

Table 1 Physical properties and ionic conductivities of different electrospun separators

Samples	PVDF	PPESK	PPESK/PVDF/PPESK		
			K:F = 2:3	K:F = 4:3	K:F = 8:3
Thickness (μm)	77	161	150	182	195
AFD (μm)	0.92	1.38	–	–	–
APS (μm)	2.21	4.23	–	–	–
Porosity (%)	88	92	–	–	–
Practical uptake (%)	444	1214	928	1079	1140
Theoretical uptake ¹⁾ (%)	444	1214	752	884	1004
Conductivity (×10 ⁻³ S cm ⁻¹)	3.91	7.29	5.42	5.94	7.35

1) Theoretical uptake = $U_{\text{PPESK}} \times M_{\text{PPESK}} + U_{\text{PVDF}} \times M_{\text{PVDF}}$, where U is electrolyte uptake of the separator

M is mass percent of the resins in PPESK/PVDF/PPESK composite separator

The ionic conductivities of different separator/electrolyte systems are listed in Table 1. It is observed that PPESK separator/electrolyte displays higher ion conductivity than PVDF separator/electrolyte due to fluffy porous structure and high electrolyte uptake of PPESK fabrics. The ionic conductivity of PPESK/PVDF/PPESK separator/electrolyte is also higher than that of PVDF separator/electrolyte. And with the increasing PPESK content, the ionic conductivity of PPESK/PVDF/PPESK separator/electrolyte increases. When the mass ratios between PPESK and PVDF is increased to 8:3, the ionic conductivity of PPESK/PVDF/PPESK separator/electrolyte is increased to $7.35 \times 10^{-3} \text{ S cm}^{-1}$, which is close to that of PPESK separator/electrolyte. Associated with practical uptake higher than theoretical uptake of PPESK/PVDF/PPESK separator, it is suggested porous structure and puffed interface between PVDF layer and PPESK layer can hold more liquid electrolyte in the composite separator. That contributes to improving ionic conductivity of PPESK/PVDF/PPESK separator/electrolyte.

3.4 Electrochemical stability

The electrochemical stability of electrospun PPESK/PVDF/PPESK composite separator containing $1 \text{ mol L}^{-1} \text{ LiPF}_6\text{-EC/DMC}$ was evaluated by linear sweep voltammetry (LSV) of Li/separator/SS cells at a scan rate of 5 mV s^{-1} over the range of 0–6 V at room temperature [30]. Figure 2 shows current–voltage curves of separator/electrolyte, and PVDF and PPESK separator/electrolyte was included for comparison. It is observed that the current of three curves keeps a stable value before the potential increased to 4.2 V. After that, the current displays an increasing tendency with the increasing of potential. The PVDF and PPESK/PVDF/PPESK separator/electrolyte systems show similar current–voltage curves. The current sharp increases at about 4.8 V, which is the electrochemical decomposition process of the two separator/electrolyte systems. While on the curve of PPESK separator/electrolyte system, the decomposition occurs at about 5.1 V. As is known, the electrochemical stability voltage of $1 \text{ mol L}^{-1} \text{ LiPF}_6\text{-EC/DMC}$ (1:1 in volume) electrolyte is about 5.15 V. It is suggested that PPESK separator has better electrochemical stability in $1 \text{ mol L}^{-1} \text{ LiPF}_6\text{-EC/DMC}$ electrolyte than PVDF separator. Anyhow, the electrochemical stability voltage of all separators is higher than 4.2 V, which is enough for the cell charge–discharge cycling. The PPESK/PVDF/PPESK composite separator could be employed to evaluated lithium-ion battery cycling process.

3.5 Thermal properties

DSC was employed to investigate the thermal properties of the separators. Figure 3 shows DSC curve of PPESK/

PVDF/PPESK composite separator, and PPESK fabrics and PVDF fabrics are also included. PPESK fabrics display excellent thermal stability property. A relatively wide endothermic peak occurs on the DSC curve of PPESK fabrics, until the sample temperature rises higher than 273°C (Fig. 3b). While for PVDF fabrics, a remarkable endothermic peak displays at about 160°C (Fig. 3a), which is the melting endothermic peak of PVDF resins. A similar endothermic peak with significant decreased intensity still exists for PPESK/PVDF/PPESK composite separator (Fig. 3c). It is indicated that the inner PVDF layer of the composite separator could melt when temperature is higher than 160°C . The melting of PVDF layer could negatively affect thermal dimensional stability of the composite separator.

The thermal dimensional stability of the separators is evaluated by thermally treated at different temperatures. Selecting appropriate treatment temperatures is important to improve the testing efficiency. Usually, the thermal dimensional stability of separators is mainly affected by the melting of polymers. For PVDF, an alpha relaxation at lower temperature (about 80°C) also could result in a shrinking of the separator [37, 38]. However, associated with electrospun PVDF fabrics dried in oven at 120°C for 6 h, the alpha relaxation might be finished. The PVDF separator would not shrink at about 80°C . Actually, in our experiment, no shrinking was observed after the electrospun PVDF separators treated at 80°C for 1 h. The PVDF separator melted and shrunk seriously after treated at 170°C for 1 h (Fig. 4b). More serious shrinkage for PVDF separator was observed at 180°C (Fig. 4c). While the PPESK separator kept its original shape even treated at 180°C for 1 h (Fig. 4e). To easily observe the shrinking of the PPESK/PVDF/PPESK composite separators, the thermal dimensional stability was

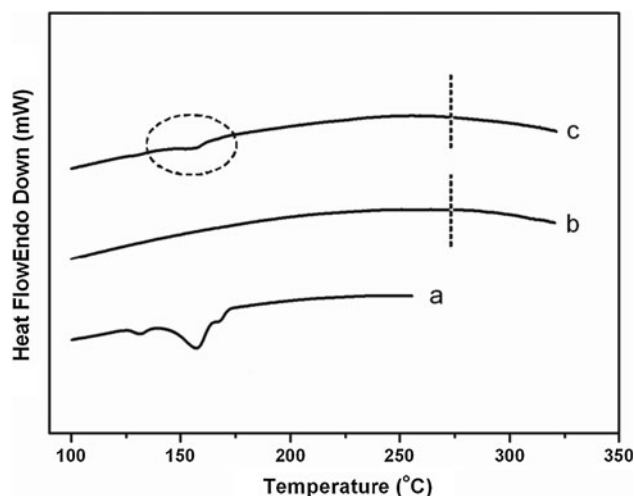


Fig. 3 DSC curves of different separators, (a) PVDF separator; (b) PPESK separator; (c) PPESK/PVDF/PPESK composite separator

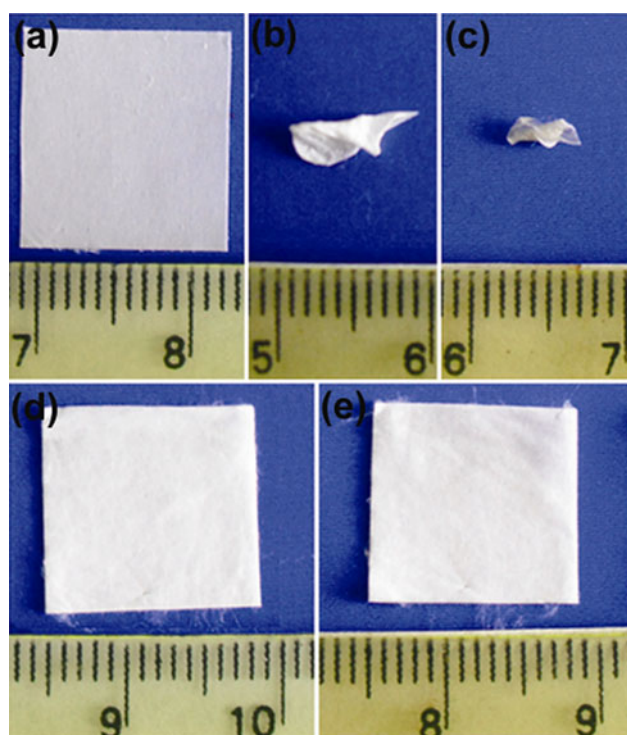


Fig. 4 Photographs of separators before and after thermal treatment at different temperature, (a)–(c) PVDF fabrics, (a) before thermal treatment, (b) 170 °C, (c) 180 °C; (d)–(e) PPESK fabrics, (d) before thermal treatment, (e) 180 °C

characterized at 180 °C for 1 h. Figure 5 shows the photographs of different PPESK/PVDF/PPESK separators before and after thermal treatment. The composite separator with relatively low content of PPESK resins (K:F = 2:3) seriously shrinks after thermal treatment, which results from the shrinking and melting of inner PVDF layer (Fig. 4c). While increasing the mass ratios of PPESK, thermal dimensional stability of composite separators is improved. When the mass ratio between PPESK and PVDF is increased to 4:3, the shape of PPESK/PVDF/PPESK composite separators is almost unchanged after thermally treated at 180 °C. Although the inner PVDF layer melts and closes up some of pores (Fig. 5c), the shrinking strength is not strong enough to deform the PPESK layers under this mass ratio. It is indicated that the PPESK/PVDF/PPESK composite separator can display excellent thermal dimensional stability even at 180 °C. Furthermore, the closed pores of inner PVDF layer could endow the composite separators with shutdown characteristic like polyolefin tri-layer composite separators—Celgard® 2325 separator (PP/PE/PP), which is benefit of improving the thermal safety of the batteries.

3.6 Electrochemical properties of the cells

To evaluate the electrochemical performances of the cells assembled with PPESK/PVDF/PPESK separators, the

composite separator of 4:3 mass ratios between PPESK and PVDF resins was selected to conduct cycle performances of the cells. For comparison, the cells with PVDF and PPESK fabrics were assembled to carry out the cycling test, respectively. Due to fluffy structure, the electrospun PPESK/PVDF/PPESK and PPESK separator could be vertically compressed when sealed in the cells. Furthermore, the compression could result in liquid electrolyte leakage, which would negatively affect battery's electrochemical properties. To minimize the negative effects from compression, all the cells were assembled under the same pressure. Figure 6 shows a comparison of initial charge and discharge curves for the test cells assembled with different separators at 0.2C rate. The three kinds of cells show similar charge and discharge curves (Fig. 6a–d). However, some difference on the curves is noticed. In Fig. 6b, the charge voltage quickly increases when the capacity of the cell with PVDF separator increases under constant current charging. In contrast, charge voltage of the cell with PPESK/PVDF/PPESK separator shows a slowly increasing tendency. During the constant voltage charging stage, the current of the cells with PVDF and PPESK/PVDF/PPESK separators steadily decreased. However, the cell with PPESK separator displays relatively unsteadily current decreasing tendency. The unstable charge current could be caused by bad-distributed current density due to the large pore size and high porosity of PPESK fabrics. Besides, it shows in Fig. 6d that the initial discharge capacity of the cell with PPESK/PVDF/PPESK separator is 143 mAh g⁻¹, which is increased by 30 % compared to the cell with PVDF separator. And the cell with PPESK separator has the highest initial discharge capacity in the three kinds of cells. Associated with the ionic conductivity and electrolyte uptake of different separators in Table 1, it is found that excellent electrolyte uptake and high ionic conductivity of PPESK separator are beneficial to improving the charge and discharge performances of the cells.

Figure 7 shows the cycling efficiency of the cells assembled with PPESK/PVDF/PPESK, PVDF and PPESK separator, respectively. The cells with the three kinds of separators have similar efficiency-cycling number curves. At initial cycles, the charge–discharge efficiency of the cells is relatively low and increases with the increasing of cycling number. After several cycles, the charge–discharge efficiency tends to 100 % and keeps stable. The solid electrolyte interface (SEI) generates on the surface of graphite anode electrode during first charge–discharge processes [39–41]. Some liquid electrolyte and effective Li⁺ are expended during SEI generation process, which results in a relatively low charge–discharge efficiency of the cells. After several cycles, the SEI has generated completely, and the charge–discharge efficiency is improved. Moreover, it is noticed that the cells with PPESK/PVDF/PPESK and PPESK separator

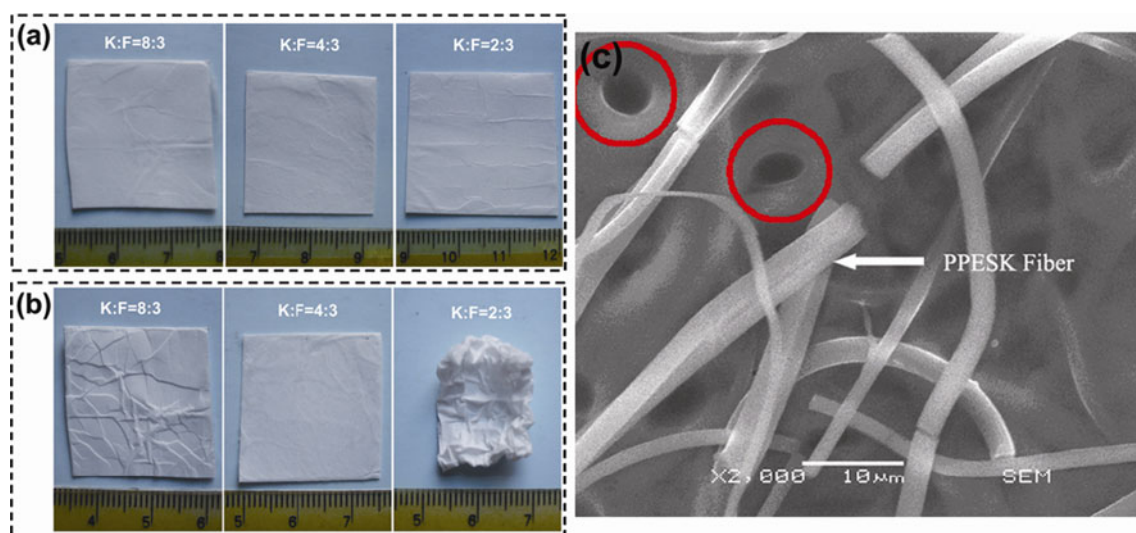


Fig. 5 Photographs of different PPSK/PVDF/PPESK separators before and after thermal treatment at 180 °C, (a) before thermal treatment, (b) after thermal treatment, (c) SEM image of PVDF inner

layer after the composite separator thermally treated at 180 °C, the red circle area shows unclosed pores

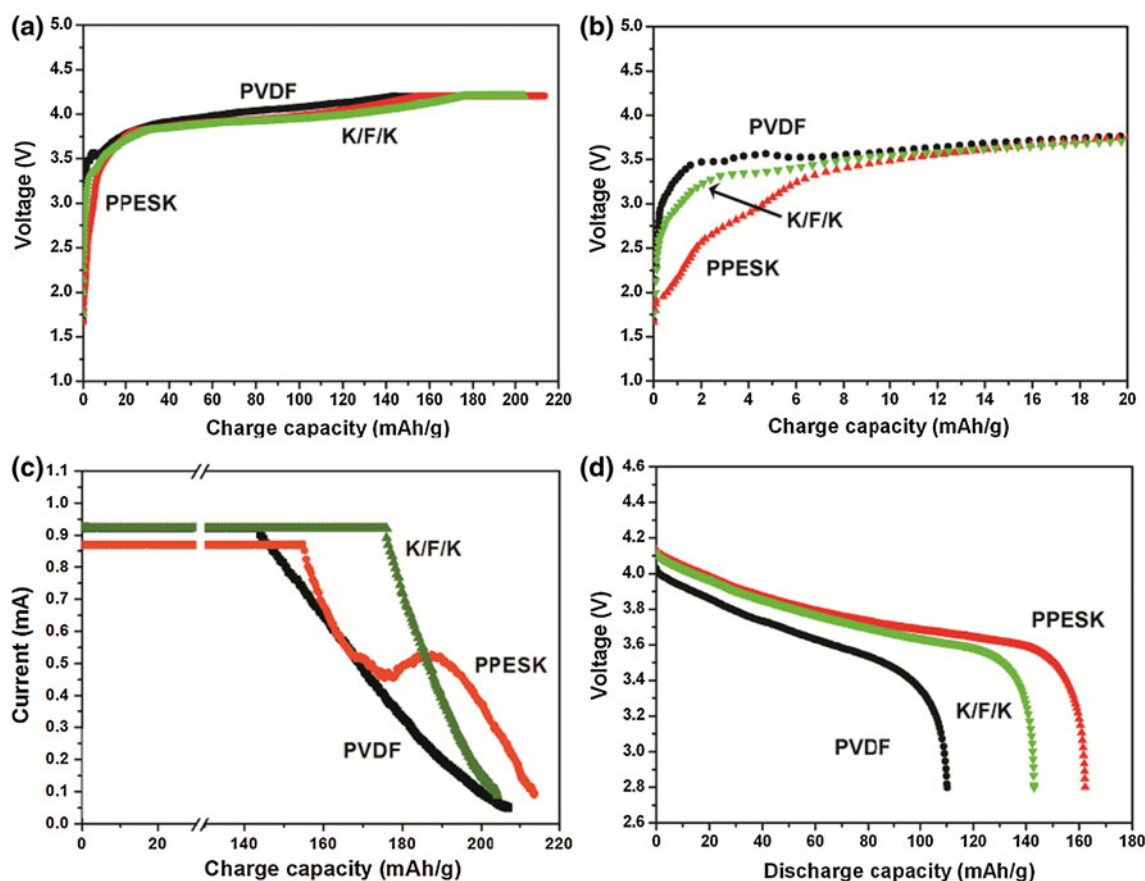


Fig. 6 Initial charge and discharge curves of the cells using different separators at 0.2 C rate, (a)–(c) charge process; (d) discharge process

have higher efficiency than that with PVDF separator at the first cycle. Associated with ionic conductivity and electrolyte uptake of the two separators, it is suggested that high

ionic conductivity and electrolyte uptake of the PPSK/PVDF/PPESK separators have positive effects on improving the cycling efficiency of the cells.

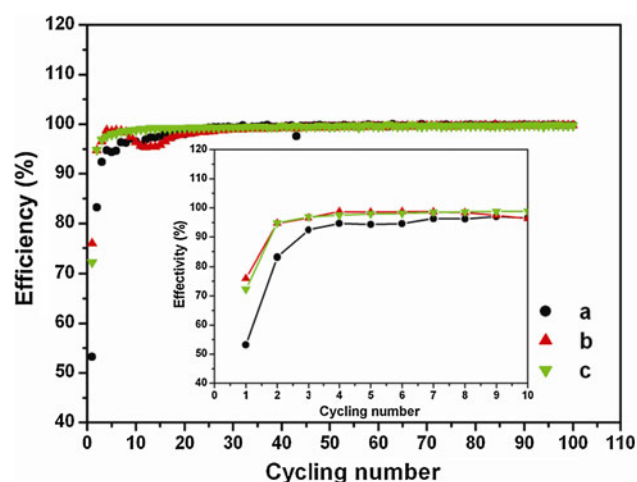


Fig. 7 Cycling efficiency of the cells with different separators, (a) PVDF separator; (b) PPESK separator; (c) PPESK/PVDF/PPESK composite separator

Figure 8 shows the discharge capacity–cycling number curves of the cells with three kinds of separators. The discharge capacity of the three cells shows similar change trend. During first cycles, the capacity slightly decreases with the increasing cycling numbers. After several cycles, the capacity tends to a stable value. The change trend of capacity agrees with that of cycling efficiency (in Fig. 7). It is suggested that the generation of SEI results in slightly decreasing capacity of the cells. In addition, it is noted that the cells with PPESK/PVDF/PPESK and PPESK separator exhibit higher discharge capacity than that with PVDF separator. After 100 times cycles, the discharge capacity of cells with PPESK/PVDF/PPESK and PPESK separator retain 137 mAh g^{-1} , which is increased by about 50 %

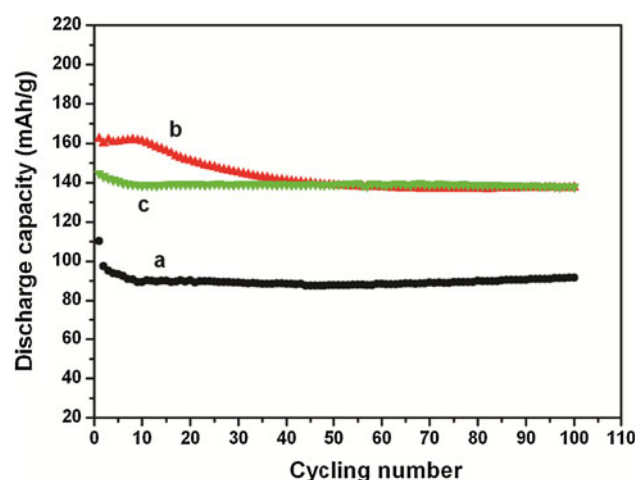


Fig. 8 Cycle performances of the cells with different separators, (a) PVDF separator; (b) PPESK separator; (c) PPESK/PVDF/PPESK composite separator

compared to that of the cells with PVDF separator. Moreover, the capacity retention rate of the cell with PPESK/PVDF/PPESK separator is 95 %, which is higher than that of the cells with PPESK separator (the capacity retention rate of PPESK separator is 85 %). Due to the introducing of PPESK resins, the PPESK/PVDF/PPESK composite separator has higher electrolyte uptake and lower resistance than PVDF separator. Taking a high hold of electrolyte solution, the PPESK/PVDF/PPESK separator can prevent capacity decreasing caused by electrolyte losses during charge–discharge cycling process. Meanwhile, compared with PPESK separator, the existence of PVDF inner layer can improve the pore structure uniformity of PPESK/PVDF/PPESK separator due to smaller pore size of PVDF fabrics, which is beneficial to forming well-distributed current density during charge–discharge process and improving the cell cycling performance. Thus, it is indicated that in the three kinds of separators, PPESK/PVDF/PPESK composite separator is more suitable for use as high performance separator in lithium-ion battery than the other kinds of separators.

4 Conclusion

Novel PPESK/PVDF/PPESK composite separators for lithium-ion battery were prepared by electrospinning technique. Due to the introducing of PPESK resins, the PPESK/PVDF/PPESK separators have higher electrolyte uptake than electrospun PVDF separator, which leads to their higher ionic conductivity than PVDF separator. Compared to the cell with electrospun PVDF separator, the initial discharge capacity of the cell with PPESK/PVDF/PPESK separator is increased by about 50 %. The charge–discharge efficiency and capacity retention rate after 100 times cycling of the cell with PPESK/PVDF/PPESK are also higher than that of the cell with electrospun PVDF separator. In addition, when the mass ratio between PPESK and PVDF resins increased up to 4:3, the PPESK/PVDF/PPESK composite separators show better thermal dimensional stability than electrospun PVDF separator. Even when the composite separators are treated in oven at 180°C for 1 h, the shape of separators is almost unchanged. It is indicated that PPESK/PVDF/PPESK composite separator is more suitable for use as high performance separator in lithium-ion battery than electrospun PVDF separator.

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